THE SEPARATION OF STABLE ISOTOPES OF CARBON BY THE COUNTER FLOW CHEMICAL EXCHANGE METHOD IN THE GASEOUS PHASE. I.

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by G. M. Panchenkov, I. A. Semiokhin, A. G. Maurina,
and N. P. Yershova

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M. Panchenkov, I. A. Semiokhin, A. G. Maurina, and N. P.
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A very effective method of separating isotopes is
that of chemical exchange carried out in a thermonuclear
column. In this method, thermal diffusion is utilized only
for the production of a counter flow between the molecules
entering into the exchange reaction.
To separate isotopes by this method, it is necessary
to select a convenient exchange reaction taking place in the
gaseous phase with a constant of equilibrium different from
one. For example, in the reaction:

$$C^{12}O_2 + C^{13}O \rightleftarrows C^{13}O_2 + C^{12}O, \qquad (1)$$
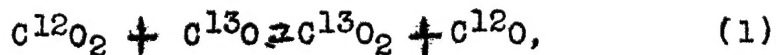
the constant of equilibrium at 25° C. is equal to 1.086.
This reaction was studied in detail by Bernstein and Taylor
/1/. The exchange of C^{13} between CO_2 and CO is carried
out in a column of the type of Clusius and Dicket /2/ in
which the cooler currents, directed downward by convection,
became enriched with the heavier CO_2 component. If the iso-
tope exchange favors the transfer of a heavy isotope into a
heavy molecule, then this isotope will be concentrated in
the cold current and carried by convection to the bottom of
the column. Bernstein and Taylor found that this enrichment
of the carbon dioxide with the C^{13} isotope increases with
the elevation of the temperature and pressure (the experiment
was conducted in the presence of steam at $PH_2O = 20$ mm of
Hg.). Under identical conditions, greater enrichment was
attained on a platinum filament than either on tungsten or
on nichrome. The authors observed an increase in the effec-
tiveness of the separation process in the presence of hydro-
gen and steam.
Urey and Brandner /3/, and Norris and Ruben /4/
who studied the excange between CO and CO_2 concluded that
nitrogen and oxygen also act as catalysts for the exchange.

1

The positive role of the addition was explained by their accelerating action on the surface of the catalyst /3,4_7, or by a change in the mechanism of the exchange in the mechanism of the exchange in comparison with the exchange without the addition /1,3_7. These authors /3,4_7 carried out experiments under static conditions, different from those of the conduction process of separating isotopes where the concentration of additions exceeds that of the exchanging gases. Experiments by Bernstein and Taylor /1,5_7 in the study of the influence of additions of hydrogen and steam, though conducted directly in connection with the process of separating isotopes of carbon dioxide, were unsystematic because they were performed with casually selected concentrations of hydrogen and of steam. That presented an interesting opportunity for investigating the influence of the addition of various gases on the exchange. The present work is directed to this problem.

Experimental Part.

The study of the process of the separation of isotopes of carbon dioxide was conducted in a thermal diffusion column (1), with an inner tube 1.0 cm in diameter and a length of 165 cm. The tube was cooled externally with water at constant temperature. Inside the reaction tube was a tightly drawn platinum wire (2) 0.5 mm in diameter, to which were welded glass "crosses" to keep it in position. To keep the wire under tension, a small glass container (3) two-thirds filled with mercury, and having a diameter of 0.8 cm and a length of 20 cm, was soldered to it with two molybdenum wires. The contact was established by means of mercury poured in a trap (4). The filament was heated by an alternating current to 800-900° C. The temperature of the filament was determined by an OPPIR-45 optical pyrometer, and by the change in the resistance of the filament. As shown in the table (page 2072) both methods gave close by agreeing values.

As its upper part, the column was connected with a reservoir whose 15-1 capacity guaranteed a supply of gas with a natural ratio of isotopes for the column.

To supply carbon dioxide from the reservoir to the column, a tubular furnace (5) was heated by an electric current to 80° C. At its lower end, the column was connected to a converter (6) in which reduction of CO_2 to CO was taking place to generate the carbon monoxide required for the exchange reaction. The converter consisted of a glass tube of 5 cm in diameter and 30 cm in length, equipped with a soldered pocket for a thermometer. Little balls prepared from zinc

2

dust and asbestos wadding were used as the reducing agent, according to the method of Bernstein and Taylor [6]. Reduction of the carbon dioxide occurred at the temperature most favorable for the conversion (390-400° C). To supply carbon dioxide from the converter to the column, a tubular electric furnace was built in and heated to 450° C.

The converter transformed almost all the CO_2 into CO, the latter moving as a stream (past the filament) upwards and exchanging with the down-moving stream of CO_2 isotopes. With the availability of a large-capacity reservoir at the top of the column, and with a complete return, the number of moles of the heavy component CO_2 entering into the column is equal to the number of moles of the light component CO leaving the upper part of the column. Under these conditions no drop in the concentration of both components occurs along the length of the column. At the same time there is a vertical isotope composition gradient. Upon attainment of equilibrium, this isotope composition gradient remains constant.

Chemically pure carbon dioxide, which occupied the column and the large reservoir prior to the start of the experiments, was prepared in an ordinary conventional type apparatus consisting of a drop funnel, flasks, two drying columns packed with $CaCl_2$ and P_2O_5, and a pressure gauge. The gas was made by the interaction of sulfuric acid and chemically pure Na_2CO_3. The system was evacuated to approximately 0.01 mm of Hg. To conduct experiments with steam in the system, a small trap was added in which a weighed amount of distilled water was introduced. Prior to evacuating the system (during the generation of the carbon dioxide), the water trap was cooled by means of liquid nitrogen.

To study the effects of the addition of various gases on the separation of the carbon isotopes, a special gas pipette was constructed (Fig 2) which allowed the entry of the additional gases into the system, in proportion to their partial pressures which was from 1 to 20 mm of Hg. Under the pressure of the carbon dioxide in the system (at 500 mm of Hg), the charging of the system with the additional gases was carried out by a branch tube of the apparatus for CO_2 generation, into which a capillary was welded for smooth entry of the gases.

Before every experiment, the entire system was evacuated to 0.01 mm, and maintained in this condition for 24 hours. Experiments were conducted only if this vacuum was maintained. The system was washed two to three times with carbon dioxide and evacuated each time to the indicated pressure, after which it was filled to the working pressure.
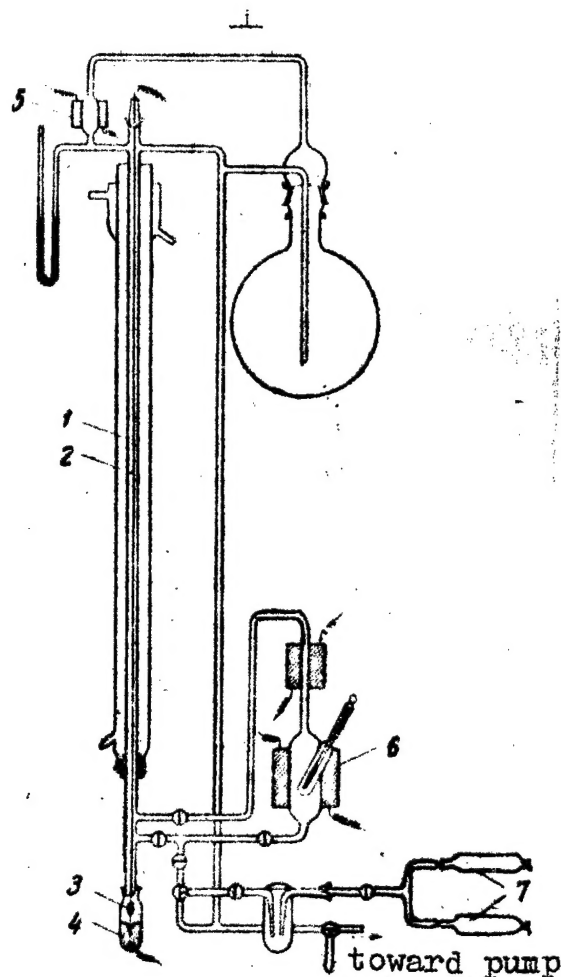
Fig 1. Apparatus for the separation of isotopes

The charging was conducted with heated furnaces and a converter (Gig 1, No. 6). The time was measured from the moment the current used to heat the filament to the necessary temperature was switched on. Each experiment was continued for four to five days. If the experiment was conducted with the addition of steam, then during the time of charging with carbon dioxide the trap was gradually heated to room temperature. The stream of dry carbon dioxide passing through the trap entrained water from it, in the form of steam, into the system. The charging of the system with the added quantities of gases to the specific pressure was done by means of a pipette (Fig 2), after filling the system with carbon dioxide to 500 mm Hg. (The reason for selecting this particular pressure will be explained below). After 2, 6, 12, 24, 48, 72, 96, and in some experiments 120 hours, samples of carbon dioxide were collected for analysis of C^{13} content, and collected in

ampoules at the base of the column. The analysis was made with a mass spectrometer of the MC-3 type. The accuracy of the analysis was kept within one to two percent of the content of C^{13} in the carbon dioxide.

Temperature of the Filament, ^{o}C

Average Value Determined by the Optical /Pyrometer_/ OPPIR-45	Determined from the Change in the Resistance of the Filament	Average Value
710	740	725
800	800	800
870	930	900

Prior to investigating the role played by the additions in the process of enrichment of the carbon dioxide with the C^{13} isotope, we conducted experiments to clarify the influence of the exchange temperature, of the material in the filaments, and of the pressure in the column. Experiments were conducted at pressures of 350, 500 and 700 mm of Hg. We determined that the enrichment on the platinum filament was greater than on the nichrome. The enrichment increases with temperature. It was found that by changing the pressure within the above limits, maximum enrichment was obtained at 500 mm. For example, in experiments conducted at 900° C (Fig 3) with a platinum filament, the enrichment was greater at 500 than at 350 and 700 mm. Similar effects were observed at 700° C, on both the platinum and nichrome filaments. These findings are somewhat contradictory to those of Bernstein and Taylor; with reference to the decrease in enrichment with increasing pressure.

However, the fact that the conclusions of these authors were based on experiments at pressures of 0.5, 1 and 1.5 atmospheres, and at intervals at which the process was not studied, allows us to hope that the accuracy of our conclusions are sound. In this connection, all our further experiments were conducted only at a pressure of 500 mm of Hg.

(Fig 2.   Gas pipette for measuring
doses of gas)

The general coefficient of enrichment was calculated according to the formula:

$$S_t = \frac{R_0}{R_t},\qquad(2)$$

where R_0 is the ratio of the peaks obtained by mass spectrometric analysis of the existing carbon dioxide. and is equal to the ratio of mole fractions of $[C^{12}O_2]/[C^{13}O_2]$ to CO_2 in carbon dioxide at $t = 0$; R_t is the corresponding ratio in a sample of carbon dioxide taken from the lower part of the column at some time t after the start of the experiment.

It is not difficult to show that under equilibrium conditions of a column with a large reservoir, the common coefficient of enrichment, calculated by the above method, is equal to the general coefficient of separation.
Indeed,

$$S_{t=\infty} = \frac{R_0}{R_{t=\infty}} = \frac{1}{R_{t=\infty}} \bigg/ \frac{1}{R_0} = \frac{[C^{12}O_2]_{t=\infty;\,h=0}}{[C^{13}O_2]_{t=\infty;\,h=0}} \bigg/ \frac{[C^{13}O_2]_{t=0}}{[C^{12}O_2]_{t=0}}$$

where h is the length of the column from which the samples are taken.

Taking into account the fact that at the upper end

6

of the column, when the system is in equilibrium, the concentration of $[C^{12}O_2]_{t=\infty; h=H}$ is equal to the concentration of $[C^{12}O_2]$ in the reservoir (that is, is equal approximately to $[C^{12}O_2]_{t=0}$, it is possible to express $S_{t=\infty}$ in the following manner:

$$S_{t=\infty} = \frac{[C^{12}O_2]_{t=\infty;\ h=0}}{[C^{12}O_2]_{t=\infty;\ h=0}} \bigg/ \frac{[C^{12}O_2]_{t=\infty;\ h=H}}{[C^{12}O_2]_{t=\infty;\ h=H}}.$$

At equilibrium, there is no gradient of concentration of both components CO and CO_2 along the column at any given height:

$$[CO] = [CO_2]; \quad [C^{12}O] = [C^{12}O_2] \ \textbf{и} \ [C^{12}O] = [C^{12}O_2].$$

If we assume this to be correct also for the upper end of the column (where h equals H), then the expression for $S_{t=\infty}$ could be given by the expression:

$$S_{t=\infty} = \frac{[C^{12}O_2]_{t=\infty;\ h=0}}{[C^{12}O_2]_{t=\infty;\ h=0}} \bigg/ \frac{[C^{12}O]_{t=\infty;\ h=H}}{[C^{12}O]_{t=\infty;\ h=H}},$$

that is, we arrive at the expression of the general coefficient for the separation of isotopes.

Therefore, in further discussion, the meaning of Sstatic $= S_{t=\infty}$, calculated according to equation (2) after reaching a steady state, will be considered as the equilibrium general coefficient of separation.
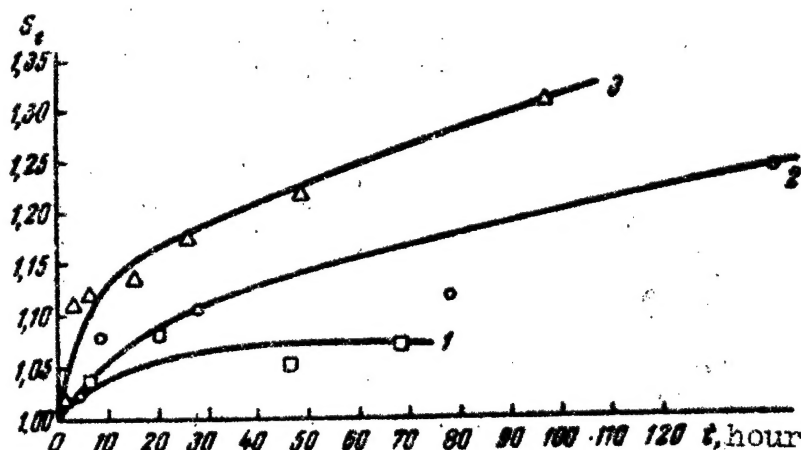

Fig 3. Dependency of the general coefficient of enrichment on the pressure in the system (Platinum filament at 900° C.) 1 = 350 mm, 2 = 700 mm, 3 = 500 mm of Hg.

Effect of steam. We conducted four experiments at steam concentrations in the system corresponding to partial pressures of 1, 3, 10, and 15 mm of Hg. The pressure of CO_2 was 500 mm. The calculations for the water necessary to develop these pressures were made according to the ideal gas laws. The duration of each experiment was four days; the temperature of the platinum kilament was 800° C. As can be seen in Figs 4 and 5, the equilibrium general coefficient of separation (of isotopes in our column) increases with an increase of steam, from $S_\infty = 1,13$ (without additions) to $S_\infty = 1,20$ (at a water pressure of 15 mm of Hg). The time needed to reach equilibrium decreases from four to five days (without additions) to one day (in the presence of steam), while remaining independent of the concentration of steam in the system.

The addition of steam increases the speed of exchange, which leads to an increase in the efficiency of the column, and to a change in the number of theoretical plates.

When the change in the coefficient of separation was determined by the velocity of isotope exchange and not by diffusion, Bernstein and Taylor [1] obtained the following ratio between the number of theoretical plates n and the constant velocity of the exchange k:

$$n = \frac{k}{v} H,$$

where v represents average convection velocity (in cm/per sec), and H is the height of the column.

In drawing conclusions from this relationship, the authors assumed that the reactions of isotope exchange are subject to first order equation relative to the presence of the rare isotope [7].
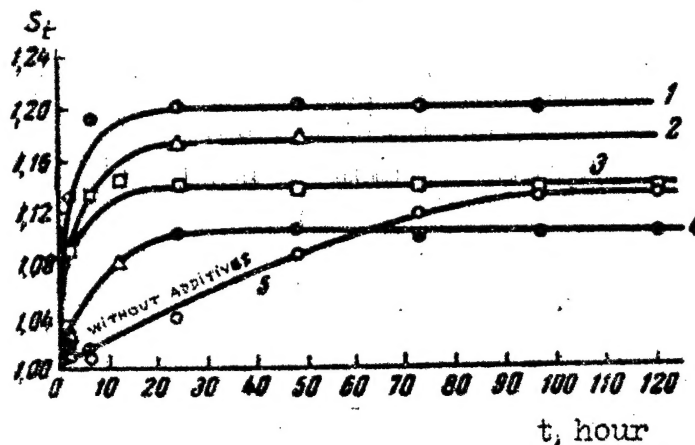
Fig 4. Dependency of the general coefficient of enrichment upon time, at the various partial pressures of steam. 1 = without addition of steam; 2 = 5 mm. steam pressure; respectively, 1, 3, 10 and 15 mm. of Hg.
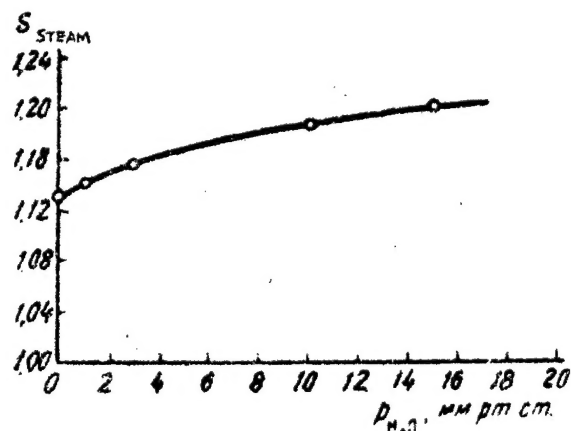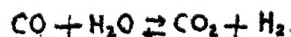

Fig 4. Dependency of the equilibrium general coefficient of separation on the partial pressure of the steam.

The acceleration in the rate of exchange of isotopes of carbon dioxide between CO_2 and CO by means of steam depends upon the predominance of the reaction:

$$CO + H_2O \rightleftarrows CO_2 + H_2$$

which, at temperatures around 800° becomes important in the oxidation of CO (8).

It is possible, too, that the accelerating action of steam on the surface of the platinum filament is a

9

contributing factor.*

Effects of hydrogen. We conducted four series of
experiments with additions of hydrogen, at partial pressures
in the system of 1, 3, 5 and 10 mm of Hg. The conditions
of the experiments were the same as those with steam. Re-
peated efforts to conduct the experiment at partial pres-
sures of hydrogen of 20 mm were unsuccessful because the
platinum filament burned out 20-30 minutes after the start
of the experiment.

Apparently, due to the high adsorbency of the hydro-
gen by the platinum wire, the latter disintegrated to such
an extent that it was unable to withstand the tension, and
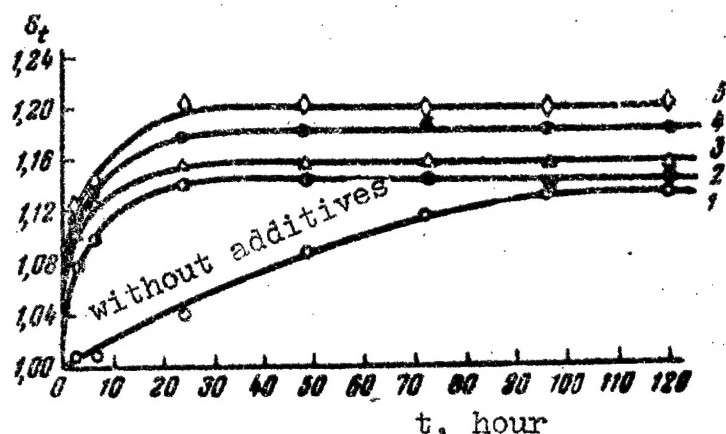hence fractured.

t, hour

Fig 6. Dependency of the general coefficient of en-
richment on time at various partial pressures of hy-
drogen. 1 = 1 mm; 2 = 3 mm; 3 = 5 mm; 4 = 10 mm Hg;
5 = without addition of H_2.

The experiment demonstrated (Fig 6) that the time
for attaining an equilibrium at the pressure of hydrogen
diminishes from 100-120 hours (in the absence of any addi-
tions to the mixture), to approximately 12 hours. The
coefficient of separation increases from 1.3 (in the
absence of additions) to 1.20 (with pressure of hydrogen
equal to one mm of Hg). However, in case of an increase

* In experiments with the addition of steam and various
gases, we were not able to determine their effect upon
thermal diffusion and the consequent effect upon the co-
lumn, even though such influences, in all probability
occur.

10

in concentration of hydrogen in the system, the coefficient
of separation gradually diminishes to 1.10 (at a pressure
of hydrogen equal to 10 mm), i. e., it appears to be even
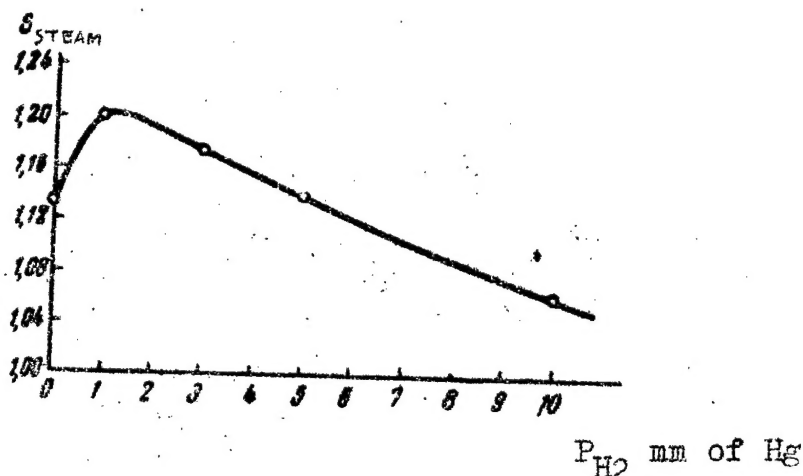smaller than in the absence of additions.

Fig 7. Dependency of the equilibrium general coeffi-
cient of separation on partial pressures of hydrogen.

The curve shown in Fig 7, indicating the dependency
of the equilibrium general coefficient of separation on
the partial pressure of hydrogen, convinces us that it is
necessary to accept the following: in the process of ex-
change of isotopes between CO and CO_2 an important role
appears to be played by the reaction:

$$CO_2 + H_2 \rightleftarrows CO + H_2O$$
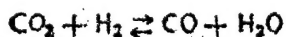
which takes place on the surface of the platinum filament.
In support of this assumption, there is the presence of a
maximum on the curve Fig 7, the exact location of which is
in the interval of 0-3 mm of Hg. Indeed, considering the
expression for the velocity of the reaction of two gases
on a surface, derived on the basis of the Langmuir equation:

$$v = \frac{k p_A p_B}{(1 + b_B p_B)^2} ,$$

it is not difficult to note that the expression with the
greater adsorbency of the gases (in our case, hydrogen)
inevitably leads to the existence of a maximum. Similar
effects were observed earlier with the hydrogenation of
carbon dioxide by hydrogen on platinum /‾9‾/.

Conclusions

1. The reaction of isotope exchange (1) taking place in a diffusion column was studied.

2. The optimum pressure of carbon dioxide for the separation of the isotopes of carbon was found to be 500 mm of Hg.

3. An increased effect in separation was obtained by the action of steam.

4. It was determined that the introduction of hydrogen into the system (in small quantities on pressure of hydrogen of the order of one mm of Hg) increases the effectiveness of the isotope separation, but that it then decreases with increased concentration of hydrogen. A theory explaining similar effects was advanced.

Moscow State University
imeni M. V. Lomonosov

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